

Characterization, monitoring and imaging of biochar by geoelectrical measurements

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Motivation and Methods

Biochar is a by-product of fuel production from organic waste and energy crops via pyrolysis or similar processes.

Biochar is also considered as a soil modifier, in particular due to

- its **fertilizing effect** and
- its **potential for long-term carbon storage**.

Thus, biochar can contribute to enhanced biomass production and to the reduction of carbon dioxide in the atmosphere. Although it has been intensively investigated since some years with various methods, there are still many open questions concerning its influence on soil properties. Methods which allow investigations in the laboratory under defined conditions and in the field are particularly interesting.

Spectral induced polarization (SIP) determines the effective complex electrical conductivity $\sigma^* = \sigma' + i\sigma''$. The real part σ' is the ohmic conductivity. The imaginary part σ'' is an additional conductivity due to polarization effects in the pore space of the soil. It provokes a phase shift between current and voltage like a capacitor in an electrical circuit.

Electrical impedance tomography (EIT) is an extension of SIP that allows imaging the spatial distribution of σ^* .

SIP and EIT are geoelectrical methods developed for large-scale application. They are known as techniques for ore exploration already since the beginning of the 20th century.

Both methods can now also favorably be used for the investigation of soil properties and processes in the vadose zone due to the considerable improvement of electronic equipment [1].

Properties of Biochars

The conditions for pyrolysis (temperature and contact time) and the hydrogen content of the biochars are very different (Table 1). The H/C molar ratio decreases with increasing temperature and contact time during pyrolysis.

Table 1: Conditions for pyrolysis and chemical composition of biochars

biochar	pyrolysis temperature / °C	pyrolysis contact time	hydrogen content / % (w/w)	carbon content / % (w/w)	H/C atomic ratio
biochar 1 from Dynamotive	450 - 500	unknown	3.37 ± 0.02	70.0 ± 1.0	0.578
biochar 2 barbecue charcoal	500	13 - 18 h	2.67 ± 0.04	87.4 ± 0.7	0.367
biochar 3 flash pyrolysis	500	1 s	3.60 ± 0.05	75.9 ± 0.3	0.569
biochar 4 gasification coke	1100	30 s	1.79 ± 0.12	83.4 ± 0.6	0.258
biochar 5 from PYREG	800	20 min	0.5	74.4	0.081

SIP Measurements on Biochars

The complex electrical conductivity σ^* was determined for mixtures of sand (grain size 125-250 μm) and 2 % biochar saturated with 4 mM NaCl solution in the frequency range from 1 mHz to 45 kHz. Spectra of the real part of the conductivity σ' and the imaginary part of the conductivity σ'' of biochar 4 are shown in Figure 1.

All biochars show an increase of the real part of electrical conductivity σ' with time indicating the release of ions from the carbon material like biochar 4 (Figure 1a).

Figure 1b shows the imaginary part of conductivity σ'' for biochar 4.

The spectra of the imaginary part of conductivity σ'' for all biochars are shown in a double logarithmic plot in Figure 2.

Figure 3 shows the time dependence of the real part of the conductivity σ' for biochar 4.

Spectra of Complex Electrical Conductivity

Biochar 4 shows high values for σ' as well as for σ'' . Both the real (Figure 1 a) and the imaginary part (Figure 1b) of conductivity are higher for the sand-biochar mixture than for sand alone. The arrow indicates the direction of the frequency change for the first half of the measurement cycle. The ohmic conductivity σ' increases during the first measurement cycle from large to low and again to high frequencies due to the release of ions.

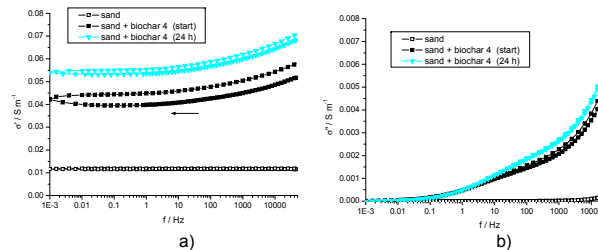


Figure 1: Real part (a) and imaginary part (b) of complex conductivity for sand and sand with 2 % biochar 4 saturated with 4 mM NaCl

Some biochars exhibit considerably lower polarization expressed by σ'' , but all values are increased above about 1 Hz (Figure 2).

The time dependence of σ' for biochar 4 is shown in Figure 3. The release of ions lasts for about 3 days. Scattering data are due to temperature effects which could not be fully compensated in a temperature range between 20 and 21 °C.

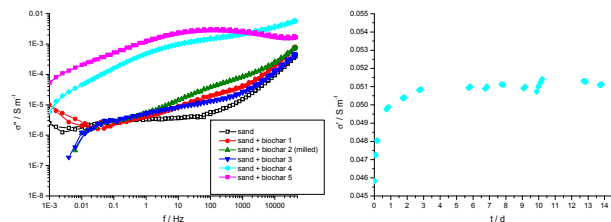


Figure 2: Spectra of σ'' for all biochars

Figure 3: Time dependence of σ' for biochar 4

Induced Polarization and H/C molar ratio

At higher frequency (above 1000 Hz), Maxwell-Wagner polarization becomes more and more important. This type of polarization is due to differences of conductivities and dielectric constants in mixtures of materials. It is particularly large, when electronic conduction is involved. Since graphite is an electronic conductor, biochar is expected to exhibit enhanced conduction compared with sand. The effect should be the larger, the more similar the biochar is to graphite.

The molar ratio of hydrogen and carbon in the biochar is a measure of carbonization. The lower this quantity is, the nearer the structure of the charcoal is to graphite. Figure 4 shows that there is a relationship between c/H molar ratio and the difference $\Delta(\sigma'')$ of the mixtures and pure sand at 2510 Hz.

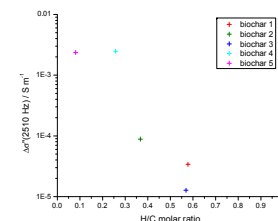


Figure 4: Correlation of the difference of σ'' between sand-biochar mixtures and pure sand at 2510 Hz and C/H molar ratio

Size Dependence of Induced Polarization

The spectra of σ'' are dependent on the size of the particles (Figure 5). Sieved fractions of biochar 2 showed a clear correlation as well as a series of commercial active carbons, but the dependence was different for both types of carbon material (Figure 6). The dependence is somewhat different from that expected for a purely diffusional process.

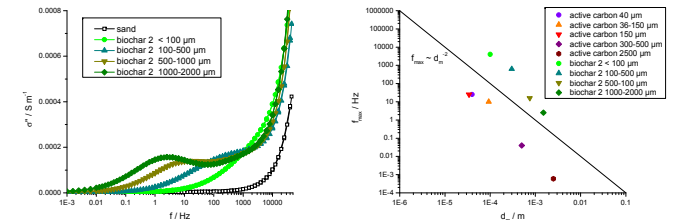


Figure 5: Spectra of σ'' for different size fractions of biochar 2

Figure 6: Size dependence of the maxima of σ'' for different size fractions of biochar 2

EIT Measurements on Gasification Coke and Active Carbon

Biochar 4 and an active carbon with similar values of σ' and different values of σ'' were used for a 2D experiment with EIT [2]. Structures of the mixtures of sand and 2 % charcoal were built into a sand matrix saturated with 4 mM NaCl (Figure 7a). The elevated σ' values of both mixtures can be well observed in the image obtained in the inversion result that used electrical measurements which were performed with a set of 16 electrodes (Figure 7b). The two different mixtures can also well be distinguished by the image of σ'' at 100 Hz (Figure 7c). Biochar 4 with its very strong polarization is well visible in the center of the cylindrical sample holder, but also active carbon with a much lower value of σ'' can be detected. The values of σ' and σ'' correspond well with those obtained by the reference SIP measurements.

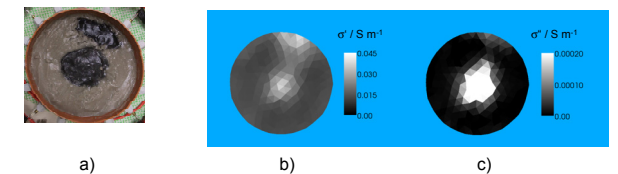


Figure 7: Photograph (a) and images of σ' (b) and σ'' (c) for a 2D-EIT experiment with sand and structures of biochar 4 (center) and active carbon (margin) at 100 Hz

Conclusions and Outlook

SIP allows the observation of processes (ion release) and the characterization of biochars concerning

- particle size and
- degree of carbonization.

EIT allows the localization of biochar in sand and most probably also in soil. It thus enables spatial resolution of processes related to biochars, e.g. ion release.

According to the results of this study, SIP and EIT are suitable to investigate special aspects of biochars in soil. Further experiments on the influence of water saturation seem to be promising for determining hydraulic parameters. Combined measurements of SIP with multistep outflow and EIT experiments on evaporation are planned. Since both methods can be applied at different scales, SIP and EIT may not only be useful for basic investigations in the laboratory, but also for long-term monitoring in the field.

References

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